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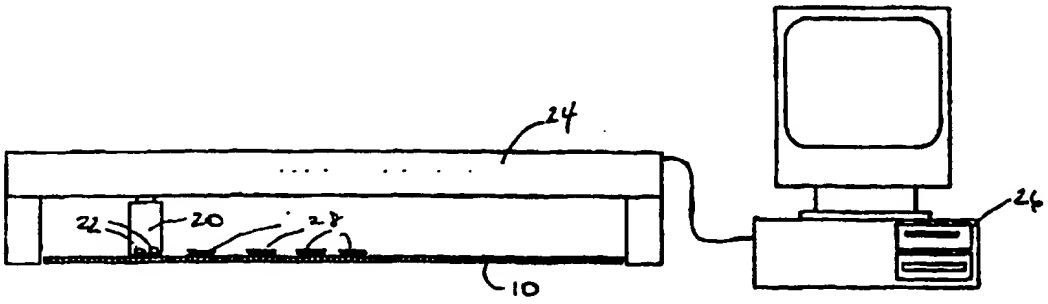

(57) Abstract

Methods and apparatus are provided for the transfer of negative images (28) directly to the surface of photo-curable relief image printing plates (10). Such negative images (28) are transferred by depositing a radiation blocking material on the plate surface with an ink jet print head (20). Following exposure to actinic radiation and further processing, those portions of the plate not lying beneath the radiation blocking material form the relief image.

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METHODS AND APPARATUS FOR PREPARING RELIEF IMAGE PRINTING PLATES

FIELD OF THE INVENTION

The present invention is directed to the formation of relief images on printing plates and, more particularly, to the direct transfer of digital images to such plates without the use of phototools or photomasks.

BACKGROUND OF THE INVENTION

Relief image printing plates are used in both flexographic and letterpress processes for printing on a variety of substrates, including paper, corrugated stock, film, foil, and laminates. Relief plates typically include a support layer and one or more layers of photocurable polymer in the form of solid sheets. The printer typically peels a cover sheet from the plate to expose the photocurable polymer and places a silver halide photographic negative or some other masking device upon the photopolymer. The printer exposes the negative-bearing plate to ultraviolet (UV) light through the negative, thereby causing exposed areas of the plate to harden, or cure. After the uncured areas of the plate are removed, cured polymer remains as the relief printing surface.

The negatives used in such processes typically are costly items, and the time required for their preparation can be considerable, particularly in those print shops that are not capable of preparing negatives in-house. Moreover, any negative which is used for printing must be nearly perfect. Even minor flaws will be carried through onto each printed

item. As a consequence, effort must be expended to ensure that the negative is precisely made. In addition, the negative is usually made with silver halide compounds which are costly and which are also the source of environmental concerns upon disposal.

Given these considerations, it is clear that any process which would eliminate the use of the negative would yield significant advantages in terms of cost, environmental impact, convenience, and image quality over known methods.

Consequently, there remains a need in the art for processes whereby relief images can be transferred to photocurable printing plates without the need for negatives or other types of phototools or photomasks.

OBJECTS OF THE INVENTION

It is one object of the present invention to provide methods for preparing photocurable printing plates that do not require the use of a phototool or photomask.

It is a further object of the invention to provide methods for transferring an electronically stored negative image directly to the surface of a photocurable printing plate.

It is yet another object of the invention to provide light-blocking compositions that can be used in transferring electronically stored images to photocurable printing plates.

It is still another object to provide apparatus that can be used to prepare photocurable printing plates.

BRIEF DESCRIPTION OF THE INVENTION

These and other objects are satisfied by the present invention, which provides methods and apparatus for the transfer of negative images directly to the surface of relief image printing plates. Such negative images preferably are transferred by depositing a radiation-blocking material on the plate surface. Following exposure to actinic radiation and further processing, those portions of the plate

not lying beneath the radiation-blocking material form the relief image.

In one aspect, the present invention provides methods for forming an image on a photocurable element by ejecting a negative-forming ink from a printer, such as an ink jet printer, onto a surface of the photocurable element. The ink preferably is substantially opaque to actinic radiation in at least one wavelength region effective to cure photocurable material within the element and substantially resistant to polymerization upon exposure to actinic radiation in the wavelength region. The ink-bearing element is exposed to actinic radiation in the wavelength region for a time and under conditions effective to cure exposed areas of the photocurable material, and unexposed (*i.e.*, uncured) areas then are removed to provide the relief printing surface.

The present invention further provides negative-bearing printing plates produced in accordance with the foregoing methods. In certain embodiments, the plates comprise a support layer, photocurable material disposed upon the support layer, and negative-forming ink disposed upon at least a portion of the surface of the photocurable material.

In another aspect, apparatus are provided for performing the methods of the invention. The apparatus comprises printing means for ejecting the negative-forming ink onto a surface of a photocurable element and exposing means for exposing the ink-bearing surface to actinic radiation to cure exposed areas of photocurable material found within the element.

BRIEF DESCRIPTION OF THE DRAWINGS

The numerous objects and advantages of the present invention may be better understood by those skilled in the art by reference to the accompanying

non-scale figures, in which:

Figure 1 is a cross-sectional view of a solid flexographic plate according to the invention.

Figure 2 is a plan view of a printing apparatus according to invention.

Figure 3 is a plan view of a printing/exposing apparatus according to invention.

Figure 4 is a cross-sectional view of a commercially-available ink jet printer.

Figure 5 is a cross-sectional view of an ink jet printer modified in accordance with the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention involves the transfer of computer-generated negative images from a printer directly to the surface of a photocurable element (*i.e.*, photocurable printing plate). There are a wide variety of photocurable elements that can be used in accordance with the invention. The photocurable elements can be solid or can include one or more liquid components. In preferred embodiments, the elements vary in thickness from about 0.025 inches to about 0.25 inches and have dimensions up to about 52 inches to about 80 inches. Solid photocurable elements can exist as cylinders or rectilinear sheets. As shown in Figure 1, a preferred photocurable element **10** comprises a support layer **12**, one or more photocurable layers **14**, **16** and a removable cover sheet **18**. Such photocurable elements optionally comprise a transparent protective layer **17** disposed between the cover sheet and the photocurable layer(s).

The support, or backing, layer can be formed from a transparent or opaque material such as paper, cellulose film, plastic, or metal. In preferred embodiments, it is a polyethylene terephthalate film having a thickness on the order of 0.005 inches. The support optionally bears an adhesive for more secure attachment to the photocurable layer.

The photocurable layer, which generally has a thickness of from about 0.02 to 0.35 inches, can include a variety of known photopolymers, initiators, reactive diluents, filler, and dyes. Preferred photocurable materials

include an elastomer compound, an ethylenically unsaturated compound having at least one terminal ethylenic group, and a photoinitiator. Exemplary photocurable materials are disclosed in European Patent Applications 0 456 336 A2 (Goss, *et al.*) and 0 640 878 A1 (Goss, *et al.*), British Patent No 1,366,769, and U.S. Patent Nos. 5,223,375 (Berrier, *et al.*), 3,867,153 (MacLahan), 4,264,705 (Allen), 4,265,986 (Allen), 4,323,636 (Chen, *et al.*), 4,323,637 (Chen, *et al.*), 4,369,246 (Chen, *et al.*), 4,423,135 (Chen, *et al.*), and 3,265,765 (Holden, *et al.*), 4,320,188 (Heinz, *et al.*), 4,427,759 (Gruetzmacher, *et al.*), 4,460,675 (Gruetzmacher, *et al.*), 4,622,088 (Min), and 5,135,827 (Bohm, *et al.*), which are incorporated herein by reference. If a second photocurable layer is used, it typically is disposed upon the first and is similar in composition but considerably thinner, usually less than 0.01 inches.

The photocurable materials of the invention should cross-link (cure) and, thereby, harden in at least some actinic wavelength region. As used herein, actinic radiation is radiation capable of effecting a chemical change in an exposed moiety. Actinic radiation includes, for example, amplified (*e.g.*, laser) and non-amplified light, particularly in the UV and infrared wavelength regions. Preferred actinic wavelength regions are from about 250 nm to about 450 nm, more preferably from about 300 nm to about 400 nm, even more preferably from about 320 nm to about 380 nm.

The protective layer, sometimes referred to as the slip film, is disposed upon the photocurable layer(s) and typically is from about 0.001 to about 0.01 inches thick. The protective layer protects the plate from contamination, increases ease of handling, and acts as an ink-accepting layer.

The final layer, the cover sheet, can be formed from plastic or any other removable material that can protect the plate from damage until ready for use.

Representative photocurable plates according to the invention include the EPIC® and SPLASH® brand flexographic

printing plates (commercially available from Polyfibron Technologies, Inc., Atlanta, GA).

A wide variety of printers can be used in accordance with the present invention. Suitable printers are those that can print (or be adapted to print) well-defined images on the various sizes and shapes of photocurable plates used in the printing industry. The level of definition (resolution) -- typically measured in dots per inch (dpi) -- should be as great as possible. The amount of ink delivered by the printers of the invention should be sufficient to absorb at least about 85% of any incident actinic radiation, preferably about 90% of such radiation, more preferably about 95%, and even more preferably 99.9% of such radiation. Preferred printers are those that are able to deliver a fully radiation-absorptive amount of ink in a single printing, although with some printers (and with some inks) multiple printings may be necessary to deliver a radiation-absorptive amount.

Ink jet printers are particularly preferred. Ink jet printing is performed by discharging ink droplets from a print head to a substrate. The droplets typically are ejected through orifices or nozzles in the print head and are directed to the substrate to form an image thereon. In contrast to many other types of printing, there usually is no contact between the printer and the substrate with ink jet printing. Virtually any ink jet printer can be used in accordance with the present invention, so long as it has both a print head and some means for controlling and/or directing the ejection of ink therefrom. Similarly, virtually any print head known in the art can be employed, so long as it comprises at least one nozzle which ejects ink droplets in response to control signals. Referring to Figure 2, a representative printing apparatus according to the present invention is shown comprising a print head 20 having a plurality of nozzles 22 and control means 24 and 26 electrically coupled with the print head. The control means can be any of those known in the art to be capable of

controlling placement of the print head relative the printing substrate and ejection of droplets from the print head. Control means amenable to the practice of this invention include computing devices such microprocessors, microcontrollers, capacitors, switches, circuits, logic gates, or equivalent logic devices. Representative control means include a personal computer coupled to a print head driver board. Representative software packages include the Adobe Photoshop and Corel Draw products. Representative ink jet printers include those manufactured by Dataproducts Corporation (Woodland Hills, CA), Jarfalla (Sweden), Encad (San Diego, CA), AlphaMerics (Simi Valley, CA), Videojet (Wood Dale, IL), particularly the Epson Stylus (Epson Corporation, Torrance, CA), HP 600c, HP 650c, HP 855c, and HP 750c ink jet printers (Hewlett-Packard Corp., Palo Alto, CA) and the Raster Image Processor (Alan Graphics, Peekskill, NY).

An ink according to present invention is any liquid or solid moiety that is both substantially opaque to actinic radiation in at least one wavelength region effective to cure the above-described photocurable elements and substantially resistant to polymerization upon exposure to actinic radiation in that wavelength region. Substantially opaque inks are those that can absorb at least about 85% of any incident actinic radiation, preferably about 90% of such radiation, more preferably about 95%, and even more preferably 99.9% of such radiation. It will be recognized that a substantially opaque ink need not be substantially opaque in all amounts and at all possible concentrations, so long as it can be deposited upon a substrate in sufficient quantity so as to be substantially opaque. Inks are substantially resistant to polymerization in accordance with the invention so long as they can be removed from the surface of plates to which they are applied (preferably using conventional plate-washing techniques) without damaging the relief surface, and so long as they do not react with or otherwise alter the chemical and/or physical properties of

the plate to such an extent that their removal damages the relief surface. Preferred inks include one or more radiation-absorptive molecules dissolved in solvent, preferably at concentrations of about 3 to about 20 weight percent. Particularly preferred inks are formed by mixing Crown Super Marking Stamping Ink (Fulton Marking Equipment Company, Warminster, PA) and UVINUL 3050 brand 2,2',4,4'-tetrahydroxybenzophenone (BASF, Ludwigshaven, Germany) in a solvent selected from methanol, isopropanol, n-butanol, chloroform, methyl ethyl ketone, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, diethylene glycol ethyl ether, and mixtures thereof. Other useful ink ingredients include the Tinopal SPF and Joncryl 68 products, which are commercially available from Ciba-Geigy Corp., Hawthorn, NY, and S.C. Johnson Company, Milwaukee, WI, respectively.

The methods of the invention involve the transfer of a negative image to the surface of a photocurable flexographic plate without use of a phototool or photomask. This typically is accomplished by removing the cover sheet from a commercially-available plate and then passing it through a printer to receive the negative image on the surface exposed by removal of the cover sheet.

After the negative image has been transferred to the surface of the photocurable element, the image is exposed to actinic radiation, preferably UV light, in a suitable wavelength region. There are many devices that can be used to expose the photocurable element, including FLEXLIGHT® brand UV modules (Polyfibron Technologies, Inc.), as well as those manufactured by Anderson & Vreeland (Bryan, OH). For certain applications, it may be desirable to combine the printing and exposing functions in a single device. In one such device, shown in Figure 3, photocurable element **10** is passed between vacuum drum **30** and print head **32** and then is passed between exposing elements **34** and **36**.

Following exposure of the negative image to actinic radiation (*i.e.*, front exposure), as well as any desired

exposure from the support side (*i.e.*, back exposure), uncured photopolymer is removed from the plate, typically by washing the plate with (and/or in) an organic and/or aqueous solvent in which the photocurable material is at least somewhat soluble. This solvent wash step typically is accompanied or preceded by brushing, wiping, or some other mild, non-destructive abrasion of the plate. Useful plate washing devices include those commercially available from Polyfibron Technologies and Anderson & Vreeland.

Additional objects, advantages, and novel features of this invention will become apparent to those skilled in the art upon examination of the following examples thereof, which are not intended to be limiting.

EXAMPLE 1

As shown in Figures 4 and 5, an HP 855c ink jet printer was modified to accept print media having thickness up to about 0.1 inches by relocating the circuit board **40**, cutting a slot **42** in the rear of the machine, modifying the pinch roll carrier plate **44**, raising the print head **46** by approximately 0.075 inches, and introducing infeed table **48**.

The printer's print cartridge was emptied, cleaned with methanol, and then refilled with a negative-forming ink having the following formulation:

Crown Super Marking Ink	35.8 wt.%
UVINUL 3050	7.7 wt %
Joncryl 68	0.5 wt %
Methanol	44.9 wt %
Propylene glycol monomethyl ether	7.8 wt %
Dipropylene glycol monomethyl ether	3.3 wt %

The ink was prepared by adding the UVINUL 3050 to the solvent mixture with stirring, and then mixing in the Crown ink. The refilled cartridge was repositioned in the modified printer.

Stock solution of an ink-accepting slip film was prepared by mixing isopropyl alcohol (50.2 wt %), water (39.8 wt %), and KLUCEL L hydroxypropyl cellulose pellets (10.0 wt %; Aqualon, Inc., Wilmington, DE). The solution was cast on a clear 5 mil MYLAR brand polyester cover sheet and dried at

room temperature for one hour. The thickness of the dried cast slip film was 0.1-0.2 mils.

An EPIC® brand flexographic printing plate having a thickness of 0.067 inches was trimmed to have a width compatible with the modified printer. The plate then was placed in a 200°F oven for approximately five minutes to preferentially increase the adhesion of the slip film present to the cover sheet. The cover sheet then was removed along with the slip film to expose the photopolymer surface. The above-cast slip film was then laminated onto the still-warm photopolymer and annealed at 150°F for two hours. The resulting plate was allowed to cool to room temperature. The clear polyester cover sheet was removed from the plate, leaving the cast slip film on the surface.

A computer-generated negative image was printed on the plate by feeding it through the printer. The printer was set at its maximum resolution of 600 dpi.

The ink-bearing plates was then flood-exposed to ultraviolet light in a FLEXLIGHT® brand UV module (Polyfibron Technologies, Inc.). The plate was back exposed for 16 seconds and face exposed for 15 minutes. The plate then was processed by applying a continuous supply of SOLVIT™ brand solvent (Polyfibron Technologies, Inc.) while brushing uncured polymer from the plate. Once all of the uncured polymer was been removed, the plate was dried at 140°F for two hours and post-exposed to germicidal UV radiation in the 200 nm to 260 nm range for a sufficient time for the plate to lose most of its tackiness. The image quality was excellent.

Conventional printing ink is applied to the negative relief surface thus produced, and the relief surface is contacted with a sheet of paper to produce a positive image. The printing is of high definition, with good ink laydown and sharp and undistorted letters.

EXAMPLE 2

An HP 850c ink jet printer was modified as described in Example 1. Also, the cartridge was modified with the ink formulation described in Example 1.

A SPLASH® brand plate having a thickness of 0.067 inches was trimmed to have a width compatible with the modified printer. The cover sheet was removed and a computer-generated negative image was printed on the resulting plate by feeding the plate through the printer. The printer was set at its maximum resolution of 600 dpi.

The ink-bearing plate was back exposed for seven seconds and face exposed for two minutes. The plate then was processed in a 1% lactic acid solution to remove the uncured polymer. The processed plate then was dried at 140°F for 60 minutes and post-cured for ten minutes to remove its tackiness. The image quality was excellent.

Conventional printing ink is applied to the negative relief surface thus produced, and the relief surface is contacted with a sheet of paper to produce a positive image. The printing is of high definition, with good ink laydown and sharp and undistorted letters.

EXAMPLE 3

An 0.067 inch thick EPIC® brand plate was placed in an AlphaMerics ink jet plotter. A image was sent to the plotter from a computer running Photoshop brand software. The plotter printed the image onto the plate at 600 DPI using a Black 4D brand solid wax ink, available from Dataproducts Corporation.

The ink-bearing plate was then exposed to UV light as in Example 1. The ink is then removed from the plate using adhesive tape, and the plate is processed using the procedure of Example 1.

Those skilled in the art will appreciate that numerous changes and modifications may be made to the preferred embodiments of the invention and that such changes

and modifications may be made without departing from the spirit of the invention. It is therefore intended that the appended claims cover all such equivalent variations as fall within the true spirit and scope of the invention.

WHAT IS CLAIMED IS:

1. A method of processing a photocurable element comprising ejecting a negative-forming ink from an ink jet print head onto a surface of said element, said ink being substantially opaque to actinic radiation in at least one wavelength region effective to cure photocurable material within said element and substantially resistant to polymerization upon exposure to actinic radiation in said wavelength region.

2. The method of claim 1 wherein said surface is a layer of photocurable material.

3. The method of claim 1 wherein said surface is a transparent protective layer disposed upon a layer of photocurable material.

4. The method of claim 1 wherein said photocurable material is disposed upon a support layer.

5. The method of claim 1 wherein said photocurable material comprises an elastomer compound, an ethylenically unsaturated compound having at least one terminal ethylenic group, and a photoinitiator.

6. The method of claim 1 wherein said photocurable element is in the form of a sheet.

7. The method of claim 1 wherein said photocurable element is in the form of a cylinder.

8. The method of claim 1 wherein said ink comprises 2,2',4,4'-tetrahydroxybenzophenone.

9. The method of claim 1 wherein said actinic radiation is ultraviolet light.

10. The method of claim 1 wherein said wavelength region is from about 300 to about 400 nm.

11. The method of claim 1 further comprising exposing said surface to actinic radiation in said wavelength region for a time and under conditions effective to cure exposed areas of said photocurable material.

12. The method of claim 11 further comprising removing uncured photocurable material from said photocurable element.

13. A photocurable element comprising:

a support layer;

photocurable material disposed upon said support layer; and

negative-forming ink disposed upon said photocurable material, said ink being substantially opaque to actinic radiation in at least one wavelength region effective to cure said photocurable material and substantially resistant to polymerization upon exposure to actinic radiation in said wavelength region.

14. The element of claim 13 wherein said photocurable material comprises a plurality of layers.

15. The element of claim 13 wherein said photocurable material comprises an elastomer compound, an ethylenically unsaturated compound having at least one terminal ethylenic group, and a photoinitiator.

16. The element of claim 13 wherein said photocurable element is in the form of a sheet.

17. The element of claim 13 wherein said photocurable element is in the form of a cylinder.

18. The element of claim 13 wherein said ink comprises 2,2',4,4'-tetrahydroxybenzophenone.

19. The element of claim 13 further comprising a transparent protective layer disposed upon said photocurable material between said ink and said photocurable material.

20. The element of claim 13 further comprising an adhesive layer disposed between said support layer and said photocurable material.

21. An apparatus for processing a photocurable element comprising:

printing means for ejecting onto a surface of said photocurable element a negative-forming ink that is substantially opaque to actinic radiation in at least one wavelength region effective to cure photocurable material within said element and is substantially resistant to polymerization upon exposure to actinic radiation in said wavelength region; and

exposing means electrically coupled with said printing means for exposing said surface to actinic radiation in said wavelength region for a time and under conditions effective to cure exposed areas of said photocurable material.

22. The apparatus of claim 21 further comprising means for removing uncured photocurable material from said photocurable element.

23. An apparatus for processing a photocurable element comprising:

at least one ink jet nozzle for ejecting ink in response to a sequence of control signals;

control means for generating said sequence of control signals; and

a photocurable element disposed opposite said nozzle and comprising a surface for receiving said ink, said ink being substantially opaque to actinic radiation in at least one wavelength region effective to cure photocurable material within said element and substantially resistant to polymerization upon exposure to actinic radiation in said wavelength region.

24. The apparatus of claim 23 wherein said surface is a layer of photocurable material.

25. The apparatus of claim 23 wherein said surface is a transparent protective layer disposed upon a layer of photocurable material.

26. The apparatus of claim 23 wherein said photocurable element further comprises a support layer adjacent said photocurable material.

27. The apparatus of claim 23 wherein said photocurable material comprises an elastomer compound, an ethylenically unsaturated compound having at least one terminal ethylenic group, and a photoinitiator.

28. The apparatus of claim 23 wherein said photocurable element is in the form of a sheet.

29. The apparatus of claim 23 wherein said photocurable element is in the form of a cylinder.

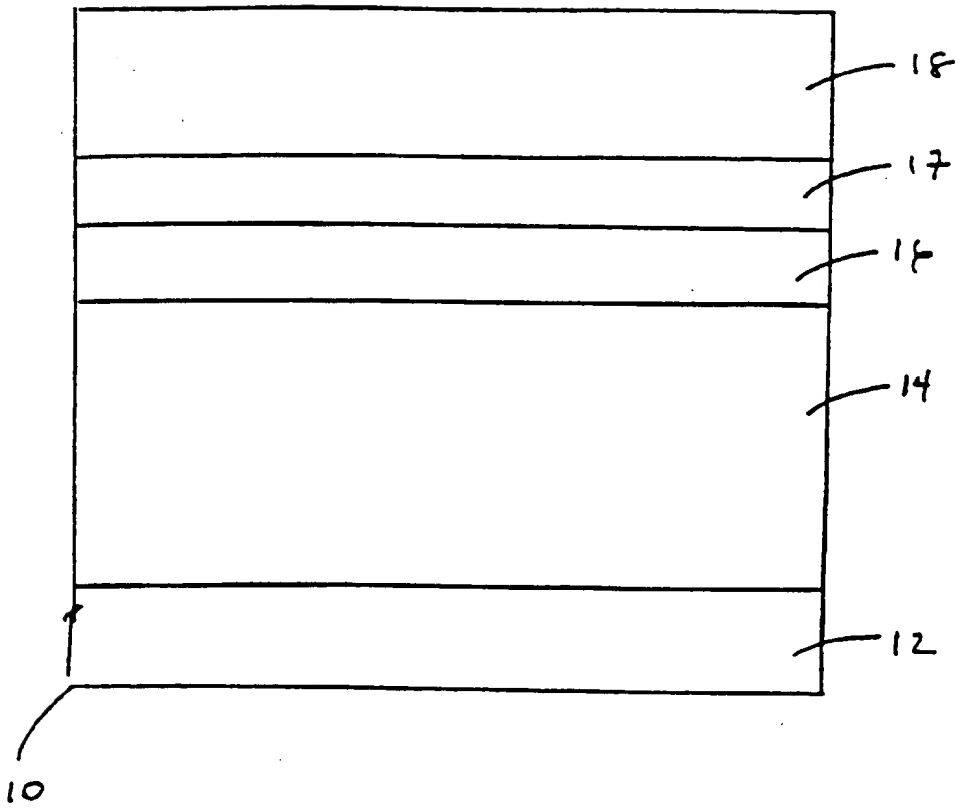

FIGURE 1

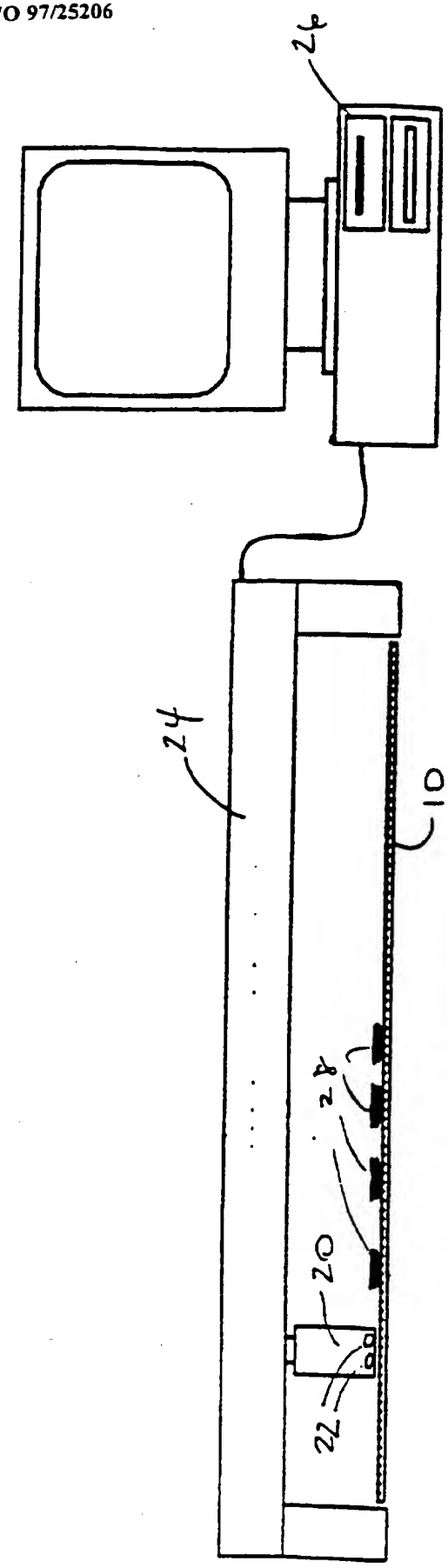

FIGURE 2

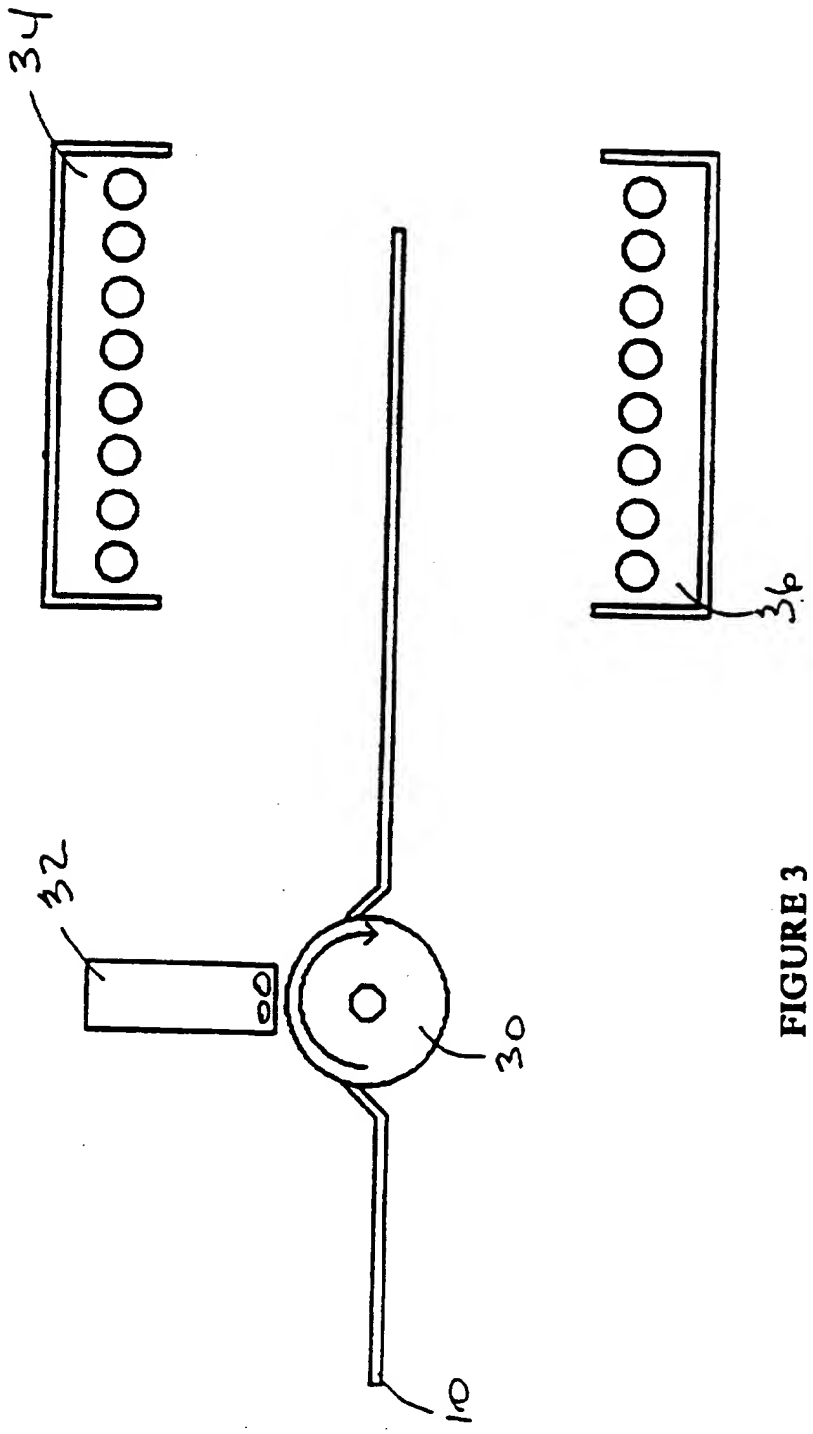

FIGURE 3

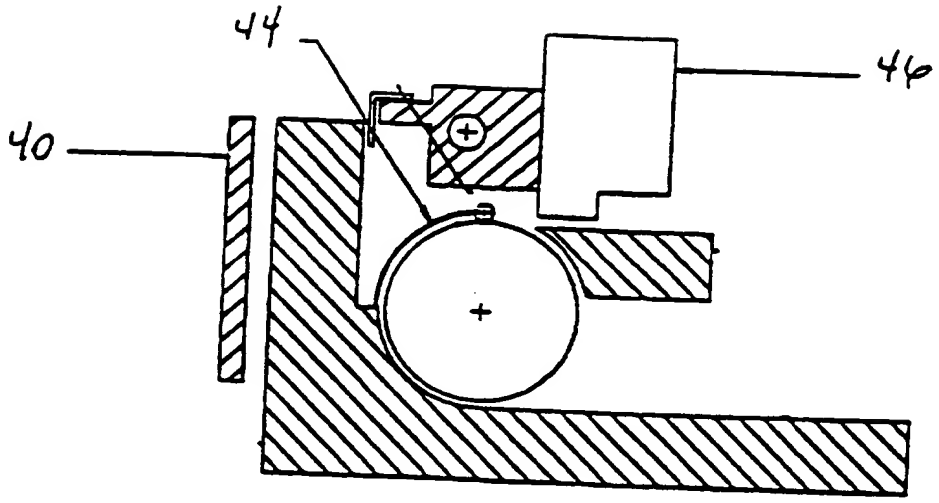

FIGURE 4

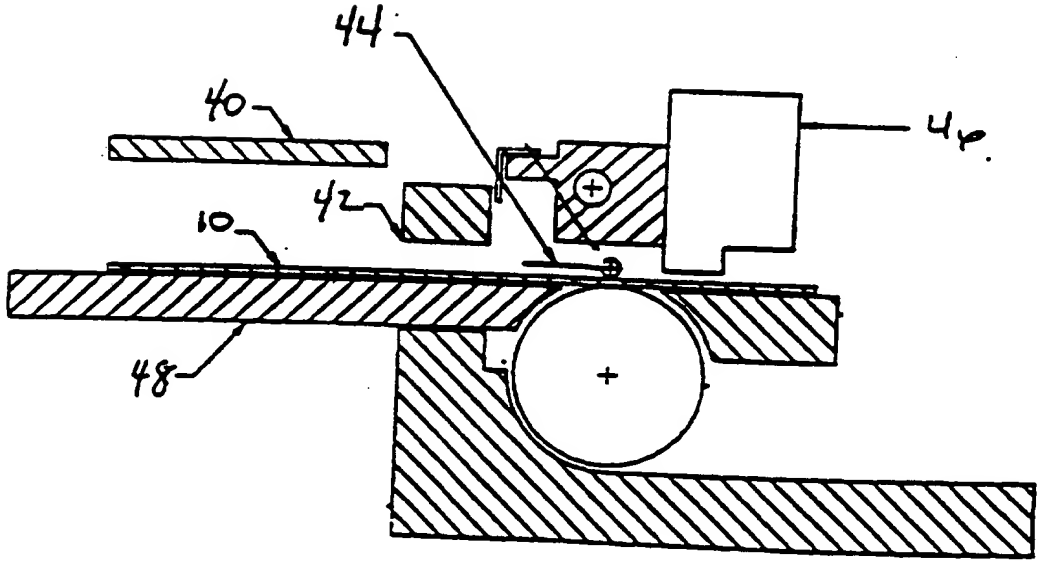

FIGURE 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US97/00182

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) :B41C 1/04; G03F 7/00
US CL :101/401.1; 430/306
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
U.S. : 101/128.4, 128.21, 396, 401.1, 456, 463.1, 465-467; 347/2; 430/306

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
APS

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	US 5,511,477 A (ADLER et al) 30 April 1996, Figs 1 and 2.	7, 17, 21
X,P ---- Y	US 5,495,803 A (GERBER et al) 05 March 1996, entire document.	1-4, 6, 7, 9, 11-13, 16, 17, 19, 23-26, 28, 29 ---------- 10
A	US 5,189,951 A (WEBSTER et al) 02 March 1993, Fig. 1.	1-29

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 5,156,089 A (McCUE et al) 20 October 1992, col. 2, lines 10-59; and col. 4, line 38 to col. 6, line 53.	1-4, 6, 9, 11-13, 16, 19, 23-26, 28 --- 10, 21, 22
Y	US 5,006,447 A (UMEDA et al) 09 April 1991, Abstract.	3, 19, 20, 25
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